SCIENCE FOR GLASS PRODUCTION

UDC 666.1

DEVELOPMENT OF COMPOSITIONS FOR GRADE A GLASSES WITH ENHANCED ILLUMINATION-ENGINEERING PROPERTIES

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The results of studies of the synthesis of barium-zirconium colorless grade A glasses, whose optical indicators are a least as good as those of lead-containing glasses, are presented. The glasses are easily made and fined at glass making temperature 1450°C. The recommended glass compositions have refractive indices 1.552 – 1.556, average dispersion (957 – 961) × 10^{-5}, and 12 – 13% (BaO + ZrO_2) content.

Key words: grade A glass, barium oxide, zirconium oxide, refractive index, average dispersion, density.

High-quality grade A glasses with enhanced refractive indices (1.53 – 1.54) and high light dispersion include, first and foremost, crystal glass. The classic composition of crystal glass contains 24%[3] PbO. At the same time this oxide is a class-1 hazard, which creates substantial ecological properties associated with lead-containing compounds being released into the environment the glass mix is prepared and loaded into the furnace, glassmaking, and mechanical working of the articles manufactured. For this reason European countries have completely rejected manufacturing articles from lead-containing crystal glasses.

The Czech glass "Bohemia" is an example of a high-quality, grade A, lead-free glass. Its illumination-engineering properties — high transparency and high refractive index — are due to high-quality raw-materials and the introduction of large oxide cations — BaO and K_2O. However, the refractive index and average dispersion of this glass are not as good as those of crystal glasses. The latter makes possible the "play of light" on the edges of the glass.

As a result, for many years, including in recent years, there has been interest in developing composition of lead-free or low-lead glasses whose refractive index (no lower than 1.53 – 1.54) and light transparency are close to those of crystal glasses but which are ecologically much more acceptable.

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[3] Here and below — content by weight.

There is a host of compositions (lead-free and low-lead) with enhanced refractive index and properties close to those of lead crystal glasses. Examples of lead-free crystal glasses are barium-lithium, barium-titanium with rare-earth element oxides, titanium-zirconium, zinc-strontium, zinc-barium-titanium, barium-titanium, zinc-barium, strontium-barium, and polytitanium (RF patents Nos. 2129100, 2137725, 210235, 2318741, 2311363, 2312825, 2304093, 2304025, 2311358, and 2311361). Barium-titanium, cadmium-titanium, and barium-zirconium compositions (RF patents Nos. 2312078, 2311362, and 2326070) have been put forth as low-lead.

The work [1] concerning the production of zirconium-containing glass with properties similar to lead and lead-barium crystal glass is of greatest interest for solving the problem of lead-free high-quality, grade A, glass. The authors proposed the following compositions of zirconium-containing glasses (%): 62.0 – 67.0 SiO_2, 3.0 – 7.0 ZrO_2, 0.1 – 0.5 B_2O_3, 1.0 – 6.0 ZnO, 8.0 – 12.0 Na_2O, 6.5 – 8.5 Na_2O, 10.0 – 12.5 K_2O with refractive index 1.537 – 1.55.

The present investigation is concerned with developing compositions of lead-free high-quality grade A glasses with refractive index and dispersion close to those of lead-containing crystal glasses but with higher chemical stability and moderate CLTE.

A. A. Appen's data [2] show that oxides (aside from rare-earth metal oxides) possess the highest partial values of the refractive index n_D and the average dispersion Δn, which are presented in Table 1.

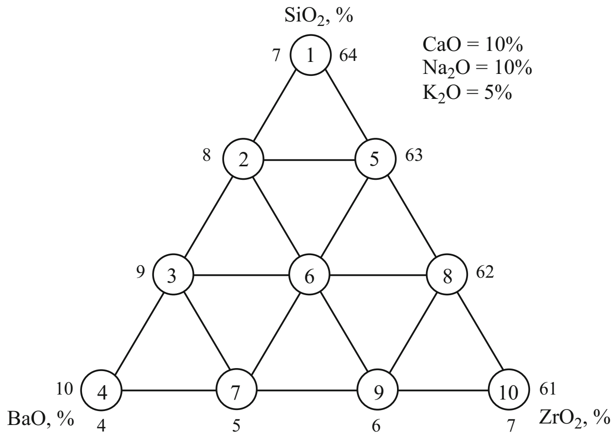

Fig. 1. Region of compositions of $Na_2O - K_2O - CaO - BaO - ZrO_2 - SiO_2$: the numbers in the circles correspond to the numbers of the glasses presented in Table 2.

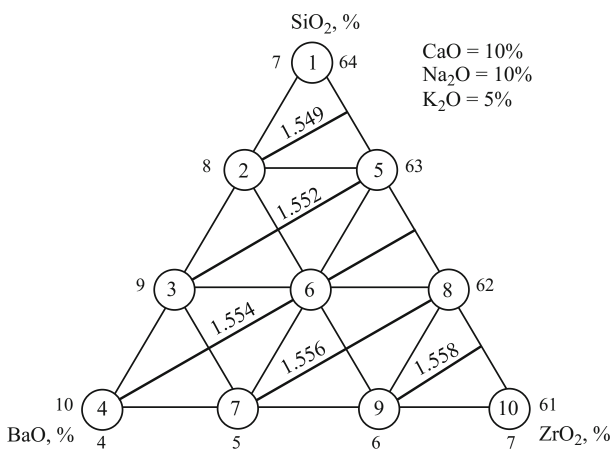

Fig. 2. Refractive index n_D of the glasses versus the composition.

Since TiO_2 imparts a color tone to glass — yellow color in an oxidative medium and brown smoky-color in a reducing medium, ZrO_2 and BaO are alternatives to PbO. But, here, the fact that BaO affects the glassmaking temperature and solidification rate of the molten glass much less than does ZrO_2 was taken into account. In addition, BaO increases the transparency of glass substantially. This made barium-zirconium glass of particular interest.

The glasses were synthesized in the system $Na_2O - K_2O - CaO - BaO - ZrO_2 - SiO_2$ in order to optimize the BaO : ZrO_2 ratio. The composition range of the experimental glasses is presented in Fig. 1.

TABLE 1.

Oxide	n_D	$\Delta n \times 10^5$
PbO	2.15 – 2.35	5280 – 7440
ZrO_2	2.20	2250
TiO_2	2.00 – 2.25	5200 – 6400
BaO	1.88	1890

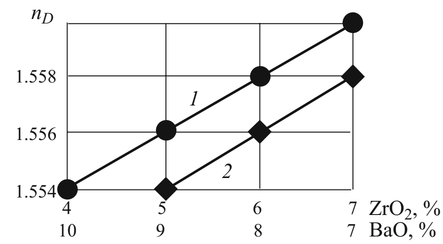

Fig. 3. Refractive index n_D of the glasses with ZrO_2 substituted for BaO: *1* and *2*) SiO_2 content 61 and 62%, respectively.

To accelerate glassmaking 1% B_2O_3 was introduced. The initial materials used were: quartz sand OOVS-015, $CaCO_3$, Na_2CO_3, K_2CO_3, KNO_3, $BaCO_3$, and TsRO-K grade ZrO_2.

The glass was synthesized in a gas furnace at 1450°C with soaking for 1 h. Well-made high-transparency glasses without any color tones were obtained. The glasses were annealed at 550°C.

The following properties of the experimental glasses were studied: softening onset temperature, density, CLTE, and water-resistance.

Limits of Variation of the Physical – Chemical Properties of Glasses in the Composition Range Studied

Softening onset temperature	600 – 620
CLTE, 10^{-7} K^{-1}	90.2 – 94.9
Density, kg/m^3	2700 – 2750
Water-resistance, mg/g	0.36 – 0.63

Appen's method was used to determine the refractive index and the average dispersion. The computed values of n_D and Δn (for compositions in molar fractions) are presented in Table 2.

It was of interest to evaluate the contribution of each oxide — BaO and ZrO_2 — to the composition dependence of the glasses (Fig. 2).

Figure 3 displays the dependence of the refractive index with ZrO_2 substituting for BaO in the system. The simultaneous introduction of BaO and ZrO_2 and decrease of the

TABLE 2.

Composition	n_D	$\Delta n \times 10^5$
1	1.547	937
2	1.549	948
3	1.552	951
4	1.554	958
5	1.552	957
6	1.554	954
7	1.556	962
8	1.556	961
9	1.558	965
10	1.560	966

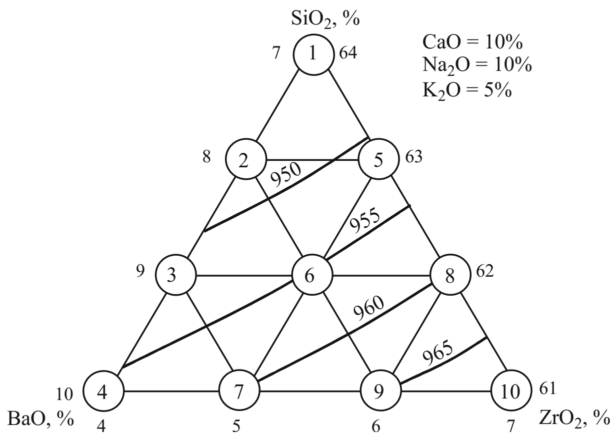

Fig. 4. Effect of the glass composition on the average dispersion ($\Delta n \times 10^5$).

SiO_2 content results in a predictable increase of the refractive index (see Fig. 2) but the fact that ZrO_2 has the predominant effect on the increase of the refractive index as compared with BaO (see Fig. 3), though their partial values $\bar{n}_D$ are practically close, draws our attention.

Together with the refractive index, as the ZrO_2 content increases, the average dispersion also increases though very little (Fig. 4).

On the basis of their indices, practically all experimental compositions can be recommended as high-quality glasses. With respect to the refractive index and the dispersion the glasses are close to lead-containing glass but they are superior to the latter with respect to chemical stability (second hydrolytic class) and have a lower CLTE. However, with respect to technological properties the glasses containing 12 – 13% (BaO + ZrO_2) with refractive index 1.552 – 1.556 and average dispersion (957 – 961) × 10^{-5} are recommended as optimal glasses.

REFERENCES

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